Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Tsubokawa, Norio and Hayashi, Shinji(1995) 'Surface Modification of Carbon Microbead by the Grafting of Polymers', Journal of Macromolecular Science, Part A, 32: 3, 525 — 535

To link to this Article: DOI: 10.1080/10601329508013681

URL: http://dx.doi.org/10.1080/10601329508013681

J.M.S.—PURE APPL. CHEM., A32(3), pp. 525–535 (1995)

SURFACE MODIFICATION OF CARBON MICROBEAD BY THE GRAFTING OF POLYMERS

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ABSTRACT

The surface grafting of polymers onto carbon microbead, a sphere of carbonized phenol resin, was achieved by two methods: 1) the radical graft polymerization initiated by azo groups introduced onto the surface and 2) the trapping of polymer radicals by a carbon microbead surface. The introduction of azo groups onto a carbon microbead surface was achieved by the reaction of surface carboxyl groups on the bead with 2,2′-azobis[2-(hydroxymethyl)-propionitrile] using *N,N′*-dicyclohexylcarbodiimide as a condensing agent. The radical polymerization of methyl methacrylate (MMA) was initiated by surface azo groups introduced onto the surface, and polyMMA was grafted onto the bead through the propagation of polymer chains from the surface: the percentage of grafting reached to 18% after 16 hours. Furthermore, it was found that by the reaction of an azo polyamide (a polyamide having an azo bond in the main chain) and peroxide polymers (polymers having peroxide groups in the main chain and/or pendant group) with carbon microbead at 70–110°C, polymer radicals formed by the thermal decomposition of these azo and peroxide polymers gave the corresponding polymer-grafted carbon microbead. The percentage of grafting decreased with increasing molecular weight of the polymer radicals. It was found that the reactivity of surface functional groups and polycondensed aromatic rings on carbon microbead are analogous with those of a carbon-black surface.

INTRODUCTION

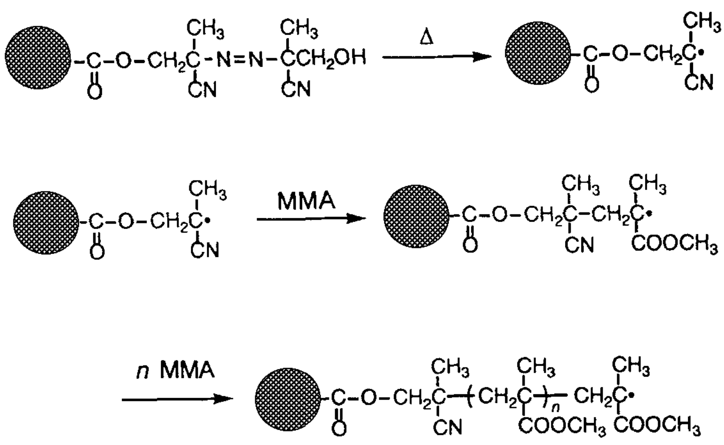
Carbon microbead, a sphere of carbonized phenol resin, has been used as an electroconductive and slipping filler of various polymers. Carbon microbead is essentially different from carbon black: although carbon blacks are made from hydrocarbons such as natural gas and oil by incomplete combustion, a carbon microbead is made from the carbonization of a microsphere of phenol resin. Differing from carbon black, carbon microbead has a spherical shape with a narrow particle size distribution, a large particle size, a small surface area, and little functional group content. The chemical reactivity of surface functional groups and polycondensed aromatic rings on carbon microbeads and the surface modification of carbon microbeads, however, have been scarcely investigated.

In a series of our papers it was reported that the surfaces of carbon black and ultrafine silica are successfully modified by the grafting of various polymers [1-3]. The dispersibility in organic solvents and polymer matrices as well as the wettability of carbon black was drastically improved by such grafting.

We pointed out that polymer-grafted carbon black with a high percentage of grafting can be obtained by the graft polymerization of monomers initiated by anionic [4, 5], cationic [6, 7], and radical [8, 9] initiating groups previously introduced onto the surface, because the propagation of grafted polymer chains starts from the surface. These initiating groups were introduced onto the surface by the conversion of surface functional groups, such as carboxyl and phenolic hydroxyl groups [4-9].

Recently, we also reported that polymer radicals formed by the decomposition of azo and peroxide polymers are effectively trapped by polycondensed aromatic rings of carbon black to give the corresponding polymer-grafted carbon black [10, 11]. This method enables us to effectively surface graft polymers with few functional groups onto carbon black.

In the present paper, to modify the carbon microbead surface, polymers are grafted onto the surface by 1) the radical polymerization of methyl methacrylate initiated by azo groups introduced onto the surface (Eq. 1) and 2) the trapping of polymer radicals formed by the decomposition of azo and peroxide polymers (Eq. 2). In addition, the reactivity of carbon microbead is evaluated.



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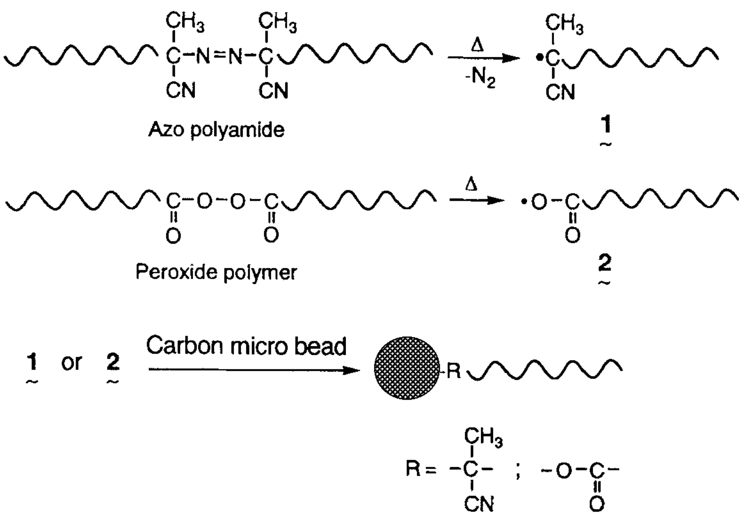

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EXPERIMENTAL

Materials

The carbon microbead (CMB-1) used was obtained from Nippon Carbon Co. Ltd., Japan, under the designation MC-0520. The specific surface area, particle size, and the content of phenolic hydroxyl, carboxyl, and quinonic oxygen groups on the bead surface are shown in Table 1. The content of phenolic hydroxyl, carboxyl, and quinonic oxygen was determined by use of 2,2-diphenyl-1-picrylhydrazyl [12], sodium bicarbonate [13], and sodium borohydride [14], respectively. The carbon microbead was dried in vacuo at 100°C before use.

Methyl methacrylate (MMA), obtained from Wako Pure Chemical Ind., Ltd., Japan, was washed with a 10% aqueous solution of sodium sulfate, aqueous alkali, and aqueous solution of sodium chloride, dried over anhydrous sodium sulfate, and distilled under reduced pressure.

2,2′-Azobis[(2-hydroxymethyl)propionitrile] (AHPN), 4,4′-azobis(4-cyanopentanoic acid) (ACPA), and *N*,*N*′-dicyclohexylcarbodiimide (DCC) were obtained from Wako Pure Chemical Ind., Ltd., Japan, and used without further purification. Diamine-terminated poly(dimethylsiloxane) (SDA: M_n = 3880) was

TABLE 1. Properties of Carbon Microbead Used

Carbon microbead	Code	Surface area, m^2/g	Particle size, μm	Functional group, mmol/g		
				OH	COOH	C=O
Untreated	CMB-1	10	5	0	0.01	0
HNO_3-treated	CMB-2	10	5	0.04	0.16	0.02

obtained from Shin-Etsu Chemical Ind. Co., Ltd., Japan, and dried in vacuo at 75°C before use.

Toluene was washed with concentrated sulfuric acid, aqueous alkali, and pure water, refluxed over sodium, and distilled. Tetrahydrofuran (THF) was refluxed over sodium and distilled. Other reagents and solvents were purified by ordinary methods.

Introduction of Carboxyl Groups onto a Carbon Microbead Surface

To introduce additional carboxyl groups onto the carbon microbead surface, the bead was treated with nitric acid. The procedures were described in detail in the preceding paper [15]. The carboxyl group content of treated carbon microbead (abbreviated as CMB-2) is also shown in Table 1.

Preparation of Azo Polyamide

Azo polyamide (a polyamide having azo bonds in the main chain) was prepared by the polycondensation of 4,4′-azobis(4-cyanopentanoic chloride) (ACPA-COCl) with SDA in the presence of triethylamine according to the method of Ueda and Nagai [17, 18]. The number-average molecular weight of the azo polyamide was estimated to be 9600 by GPC using polystyrene standards.

Peroxide Polymers

Peroxide polymers (vinyl polymers having terminal and/or pendant peroxide groups) were obtained from Nippon Oil and Fats Co. Ltd., Japan. These peroxide polymers can be prepared by the radical polymerization of vinyl monomers using 1,1-bis(*t*-butyldioxy)cyclohexane (Perhexa-C), poly(eicosanedioyl peroxide) (LC-2), and poly(triethylene glycol peroxyadipate) (ATPPO) as initiator [19, 20]. The properties of peroxide polymers are shown in Table 2.

TABLE 2. Properties of Peroxide Polymers

Peroxide polymer	Code	Initiator	$\overline{M}_n \times 10^{-3}$	f^a
Polystyrene	PPSt-1	Perhexa-C[b]	3.6	0.56
Polystyrene	PPSt-2	Perhexa-C[b]	7.3	0.42
Polystyrene	PPSt-3	LC-2[c]	15.2	0.57
PolyMMA	PPMMA-1	ATPPO[d]	15.7	1.9
PolyMMA	PPMMA-2	ATPPO[d]	20.2	1.1
PolyMMA	PPMMA-3	ATPPO[d]	51.4	2.3

[a] Functionality: f = peroxide group (mol)/polymer chain (mol).

[b] 1,1-Bis(*t*-butyldioxy)cyclohexane.

[c] Poly(eicosandioyl peroxide).

[d] Poly(tetramethylene glycol peroxyadipate).

Introduction of Azo Groups onto a Carbon Microbead Surface

The introduction of azo groups onto a carbon microbead surface was achieved by the reaction of surface carboxyl groups with AHPN using DCC as a condensing agent. A typical example follows. Into a 200-cm^3 flask, 3.0 g carbon microbead, 2.9 g AHPN, 1.2 g DCC, and 100 cm^3 THF were charged. The reaction mixture was stirred with a magnetic stirrer at room temperature under nitrogen. After 8 hours the reaction mixture was centrifuged and the sedimented carbon microbead was washed with THF and methanol repeatedly. The resulting carbon microbead was dried in vacuo at room temperature and stored in the dark below 0°C.

Graft Polymerization of MMA

Into a glass ampule, 0.30 g carbon microbead having surface azo groups and 10.0 cm^3 MMA were charged. The ampule was cooled by liquid nitrogen, thawed three times, and sealed in vacuo. The sealed ampule was heated at 70°C with shaking. After a definite time, the product was poured into a large excess of methanol. The precipitate was filtered and dried in vacuo at 60°C. The conversion was calculated by the following equation:

$$\text{Conversion}\,(\%) = (A/B) \times 100$$

where A = precipitate (g) − carbon microbead used (g)
B = monomer used (g)

Grafting Reaction of Carbon Microbead with Azo and Peroxide Polymers

Into a 100 cm^3 flask, 0.30 g carbon microbead, 5.0 g azo polyamide (or 1.0 g peroxide polymer), and 20.0 cm^3 toluene as a solvent were charged, and the reaction mixture was stirred with a magnetic stirrer under nitrogen. After a definite time, the reaction was stopped by cooling the flask to room temperature.

Percentage of Grafting

To isolate polymer-grafted carbon microbead, the reaction product was dispersed in toluene and the dispersion was centrifuged. Then the precipitated carbon microbead was extracted with THF by using a Soxhlet apparatus. The percentage of grafting was calculated by the following equation:

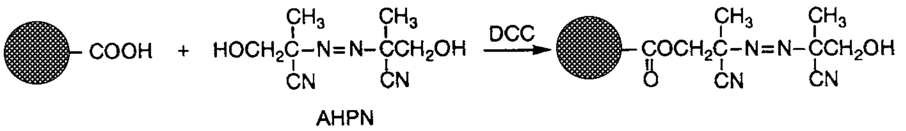
$$\text{Grafting}\,(\%) = (A/B) \times 100$$

where A is the amount of polymer grafted and B is the carbon microbead charged. The amount of grafted polymer was estimated from the weight increment of carbon microbead after the reaction.

RESULTS AND DISCUSSION

Introduction of Azo Groups onto a Carbon Microbead Surface

Although, as mentioned above, the reactivity of carboxyl groups on carbon microbead has been little reported, it is expected that the reactivity of functional groups on the surface is analogous with that of carbon black. Therefore, we examined the introduction of azo groups onto a carbon microbead surface by the reaction of surface carboxyl groups on the bead with hydroxyl groups of AHPN using DCC as a condensing agent (Eq. 3).



$$-\text{COOH} + \text{HOCH}_2\underset{\text{CN}}{\overset{\text{CH}_3}{\text{C}}}-\text{N}=\text{N}-\underset{\text{CN}}{\overset{\text{CH}_3}{\text{C}}}\text{CH}_2\text{OH} \xrightarrow{\text{DCC}} -\underset{\text{O}}{\overset{}{\text{C}}}\text{OCH}_2\underset{\text{CN}}{\overset{\text{CH}_3}{\text{C}}}-\text{N}=\text{N}-\underset{\text{CN}}{\overset{\text{CH}_3}{\text{C}}}\text{CH}_2\text{OH} \quad (3)$$

AHPN

Untreated carbon microbead (CMB-1) and HNO_3-treated carbon microbead (CMB-2) were treated with an excess of AHPN in the presence of DCC at room temperature. After purification of the treated carbon microbead, the amount of azo groups introduced onto the surfaces was determined by elemental analysis. The results are shown in Table 3.

As shown in Table 3, even if carbon microbeads are treated with AHPN in the absence of DCC, no azo groups were introduced onto the surface. On the contrary, azo groups are successfully introduced onto carbon microbead by the treatment of carbon microbead with AHPN in the presence of DCC as a condensing agent. In addition, the amount of azo groups introduced onto the surface was found to increase remarkably by use of CMB-2, i.e., HNO_3-treated carbon microbead.

Based on the above results, it is concluded that azo groups are immobilized onto a carbon microbead surface with ester bonds by the reaction (condensation) of surface carboxyl groups with hydroxyl groups of AHPN as shown in Eq. (3). Therefore, the reactivity of carboxyl groups on carbon microbeads was found to be analogous with that of a carbon black surface.

Graft Polymerization of MMA Initiated by Azo Groups Introduced onto a Carbon Microbead Surface

The polymerization of MMA was carried out in the presence of carbon microbead having azo groups at 70°C. The results are shown in Table 4.

The thermal polymerization of MMA proceeded even in the absence of carbon microbead, though the polymerization rate was very small. The polymerization of MMA was remarkably retarded in the presence of untreated (CMB-1) and HNO_3-treated carbon microbead (CMB-2); HNO_3-treated carbon microbead especially

TABLE 3. The Amount of Azo Groups Introduced onto Carbon Microbead Surface

Carbon microbead (g)	AHPN, g	DCC, g	Azo group, mmol/g
CMB-1 (3.0)	2.9	0	0
CMB-1 (3.0)	2.9	1.2	Trace
CMB-2 (3.0)	2.9	0	0
CMB-2 (3.0)	2.9	1.2	0.13

TABLE 4. Polymerization of MMA Initiated by Azo Groups Introduced onto a Carbon Microbead Surface[a]

Carbon microbead	Conversion, %	Grafting, %
None	1.4	–
CMB-1	0.3	Trace
CMB-2	0	–
CMB-Azo 1[b]	Trace	Trace
CMB-Azo 2[c]	3.3	13.2

[a] Carbon microbead (CMB-1), 0.30 g; MMA, 10.0 cm^3; 70°C; 8 hours.

[b] Prepared from CMB-1.

[c] Prepared from CMB-2.

completely inhibited the polymerization. On the contrary, the polymerization of MMA was initiated in the presence of carbon microbead having azo groups (CMB-Azo 2), and polyMMA was grafted onto the surface. This indicates that the polymerization is initiated by radicals formed by the decomposition of surface azo groups on carbon microbead. No polymerization of MMA was observed in the presence of CMB-Azo 1 because of the low content of azo groups of the surface.

Figure 1 shows the time vs conversion curve and time vs percentage of surface grafting curve for the polymerization of MMA initiated by azo groups introduced onto carbon microbead (CMB-2). It is apparent that the conversion increases linearly with the progress of polymerization. The percentage of surface grafting of polyMMA also increased during the initial stage of polymerization, but the increase became small with the progress of polymerization.

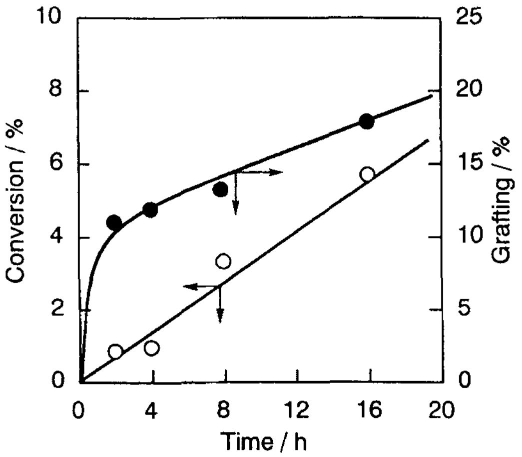


FIG. 1. Polymerization of MMA initiated by azo groups introduced onto a carbon microbead surface. CMB-Azo 2, 0.30 g; MMA, 10.0 cm^3; 70°C.

Figure 2 shows the relationship between grafting efficiency, proportion of grafted polymer to total polymer formed, and conversion in the polymerization shown in Fig. 1. It was found that grafting efficiency is about 40–50% in the initial stage of polymerization but decreases with the progress of polymerization. This indicates that although the polymerization of MMA is initiated from surface radicals and fragment radicals, initiation by surface radicals is shielded with the progress of polymerization. This may be because further polymerization due to the surface radicals formed by the decomposition of azo groups is gradually blocked by surface-grafted polyMMA chains.

Based on the above results, it is concluded that the graft polymerization of MMA is initiated by radicals formed by the decomposition of azo groups introduced onto the carbon microbead surface and that polyMMA is grafted onto the surface through the propagation of polymer chains from the surface.

Grafting Reaction of Azo Polyamide with Carbon Microbead

It is well known that carbon blacks (polycondensed aromatic rings) act as effective radical trapping agents because the reactivity of radicals to aromatic compounds increases with an increase in the number of aromatic ring [21, 22]. In the previous paper we reported that polymer radicals formed by the decomposition of azo and peroxide polymers are effectively trapped by the carbon black surface to give polymer-grafted carbon blacks with a high percentage of grafting [10, 11]. It is expected that polycondensed aromatic rings on carbon microbead also have the ability to trap free radicals. Therefore, the grafting of polymers onto a carbon microbead (CMB-1) surface by the reaction of azo polyamide and peroxide polymers with carbon microbead in toluene was examined. The results are summarized in Table 5.

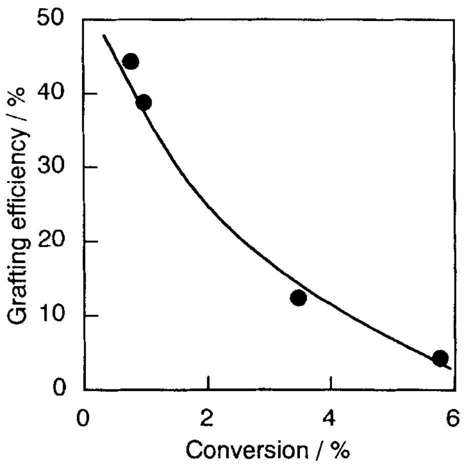


FIG. 2. Relationship between grafting efficiency and conversion in the graft polymerization shown in Fig. 1.

TABLE 5. Grafting Reaction of Carbon Microbead with Azo Polyamide under Several Conditions[a]

Polymer	Temperature, °C	Grafting, %
SDA	70	0
Azo polyamide	10	0
Azo polyamide	70	19.5

[a] Carbon microbead, 0.30 g; azo polyamide, 5.0 g; toluene, 20.0 cm^3; 5 hours.

As is seen in Table 5, even if carbon microbead were heated with SDA, no grafting onto the surface was observed. The grafting of polymers onto the surface hardly proceeded when the reaction was carried out at 10°C, at which the azo polymers hardly decompose. On the contrary, when carbon microbeads were heated with azo polyamide in toluene at 70°C, the grafting of polymers onto the surface was found to proceed. These results indicate that polymer radicals formed by the thermal decomposition of azo polyamide were successfully trapped by the carbon microbead surface as shown in Eq. (2).

The percentage of grafting onto carbon microbead was smaller than that onto a carbon black surface. This may be due to the smaller surface area of carbon microbeads.

Figure 3 shows the relationship between reaction time and percentage of grafting in the reaction of carbon microbead (CMB-1) with azo polyamide at 70°C. The grafting of polymers onto the surface increased with the progress of the reaction, and it no longer increased after about 15 hours. This may be due to the fact that the carbon microbead surface was blocked by the grafted polymer chains.

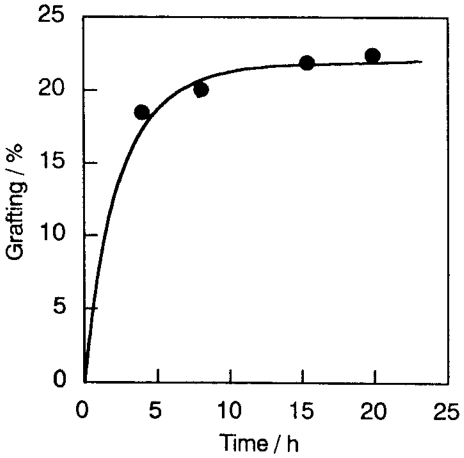


FIG. 3. Grafting reaction of a carbon microbead with azo polyamide in toluene. Reaction conditions are given in Table 5.

TABLE 6. Grafting Reaction of Carbon Microbead with Peroxide Polymers[a]

Peroxide polymer	$\overline{M}_n \times 10^{-3}$	Temperature, °C	Grafting, %	$\overline{G}_n$,[b] μmol/g
PPSt-1	3.6	110	15.8	43.9
PPSt-2	7.3	110	19.1	26.2
PPSt-3	15.2	70	14.8	9.7
PPMMA-1	15.7	70	20.3	12.9
PPMMA-2	20.2	70	11.9	5.9
PPMMA-3	51.4	70	14.4	2.8

[a] Carbon microbead (CMB-1), 0.30 g; peroxide polymer, 1.0 g; toluene, 20.0 cm^3; 6 hours.

[b] Number of grafted polymer chain estimated from the molecular weight of peroxide polymer.

Grafting Reaction of Peroxide Polymers with Carbon Microbead

Table 6 shows the results of the grafting of vinyl polymers by the reaction of peroxide polymers with carbon microbead (CMB-1) at 70 and 110°C.

It is apparent that by the reaction of peroxide polymers with carbon microbead, the vinyl polymers are effectively grafted onto the carbon microbead surface. This indicates that polycondensed aromatic rings of carbon microbead also have an ability to trap polymer radicals.

The percentage of polyMMA grafting onto the surface and the number of grafted polymer chains (G_n) decreases with increasing molecular weight of peroxide polymers. This may be because the surface aromatic rings of carbon microbead are shielded by neighboring grafted polymer chains. This effect on grafting is enhanced by an increase in the molecular weight of the polymer.

CONCLUSIONS

1. Azo groups were successfully introduced onto the carbon microbead surface by the reaction of surface carboxyl groups with hydroxyl groups of AHPN in the presence of DCC.
2. The radical graft polymerization of MMA was initiated by surface azo groups, and polyMMA was grafted onto the surface through the propagation of polymer from the surface radicals formed by the decomposition of azo groups.
3. Polymer radicals formed by the thermal decomposition of azo polyamide and peroxide polymers were effectively trapped by the carbon microbead surface to give the corresponding polymer-grafted carbon microbead.
4. The reactivity of functional groups and the radical trapping ability of polycondensed aromatic rings on carbon microbeads are analogous with those on a carbon black surface.

ACKNOWLEDGMENTS

We thank Nippon Carbon Co., Ltd., Japan; Nippon Oil and Fats Co., Ltd.; and Wako Pure Chemical Ind., Ltd. for providing the carbon microbead, peroxide polymers, and AHPN and ACPA, respectively.

REFERENCES

[1] N. Tsubokawa and T. Endo, *Tanso, 140*, 322 (1989).
[2] N. Tsubokawa, *Hyoumen, 28*, 286 (1990).
[3] N. Tsubokawa, *Prog. Polym. Sci., 17*, 417 (1992).
[4] N. Tsubokawa, *J. Macromol. Sci.—Chem., A24*, 763 (1987).
[5] N. Tsubokawa, A. Funaki, Y. Hada, and Y. Sone, *J. Polym. Sci., Polym. Chem. Ed., 20*, 3297 (1982).
[6] N. Tsubokawa, *Ibid., 22*, 1514 (1984).
[7] N. Tsubokawa and S. Handa, *J. Macromol. Sci.—Pure Appl. Chem., A30*, 277 (1993).
[8] N. Tsubokawa, K. Fujiki, and Y. Sone, *Polym. J., 20*, 213 (1988).
[9] K. Fujiki, N. Tsubokawa, and Y. Sone, *Ibid., 22*, 661 (1990); *J. Macromol. Sci.—Chem., A28*, 715 (1991).
[10] N. Tsubokawa and K. Yanadori, *Kobunshi Ronbunshu, 49*, 865 (1992).
[11] N. Tsubokawa and S. Handa, *J. Jpn. Soc. Color Mater., 66*, 468 (1993).
[12] K. Ohkita and N. Tsubokawa, *Carbon, 10*, 631 (1972).
[13] D. Rivin, *Rubber Chem. Technol., 36*, 729 (1963).
[14] S. Suzuki and K. Miyazaki, *Nippon Kagaku Zasshi, 88*, 299 (1967).
[15] K. Ohkita, N. Tsubokawa, S. Sekine, and T. Yamada, *Nippon Gomu Kyokaishi, 47*, 40 (1974).
[16] N. Tsubokawa and T. Yoshihara, *J. Polym. Sci., Polym. Chem. Ed., 31*, 2459 (1993).
[17] A. Ueda and S. Nagai, *Ibid., 24*, 405 (1986).
[18] H. Inoue, A. Ueda, and S. Nagai, *Ibid., 26*, 1077 (1988).
[19] T. Yamamoto, K. Aoshima, H. Ohmura, Y. Moriya, N. Suzuki, and Y. Oshibe, *Polymer, 32*, 19 (1991).
[20] T. Yamamoto, H. Ohmura, N. Suzuki, Y. Oshibe, and M. Sugiura, *Nippon Kagaku Kaishi*, p. 1269 (1992).
[21] D. Hey and G. Williams, *Discuss. Faraday Soc., 14*, 216 (1953).
[22] M. Levy and M. Szwarz, *J. Chem. Phys., 22*, 1621 (1954).

Received May 13, 1994
Revision received July 18, 1994